BYU

# Predicting Microstructure and Performance for Optimal Cell Fabrication

Dean R. Wheeler and Brian A. Mazzeo
Brigham Young University
June 9, 2016

Project ID # ES220

This presentation does not contain any proprietary, confidential, or otherwise restricted information

# OVERVIEW

## Timeline

- Project start date: Apr 2013
- Project end date: Mar 2017
- Percent complete: 75%

## Budget

- Total project funding: $794,000
  - (DOE share 100%)
- Funding received in FY15: $198,500 (12 months)
- Funding for FY16: $198,500 (12 months)

## Barriers

- Cell performance
  - 200 Wh/kg (EV requirement)
- Life
  - 3000 cycles (PHEV 40 mile requirement)
  - Calendar life: 15 years.
- Cost

## Partners

- Industrial collaborations with A123, Hydro-Québec, LG Chem, Bosch
- Research collaborations with LBNL, ANL, and others

# RELEVANCE

- Program Objectives:
  - Develop rapid and reliable tools for measuring and predicting electronic and ionic conductivities and 3D microstructures of particle-based electrodes
  - Understand tradeoffs and relationships between fabrication parameters and cell performance

- Current-Year Objectives:
  - Use DPP model to simulate the changes in microstructure during the electrode calendering process
  - Measure local conductivity of battery electrode films using N-line probe, including anisotropic behavior
  - Begin integrating the modeling and diagnostic elements of the project

- Impact on DOE Barriers for EVs/PHEVs:
  - This work addresses a longstanding unmet industry need to be able to conveniently quantify conductivities of thin-film electrodes and current collector contact resistance—solving this problem will accelerate process improvement.
  - This work remedies our poor understanding of the influence of fabrication parameters on heterogeneities in microstructure, which affect cell energy, power, and cycle life.

# MILESTONES

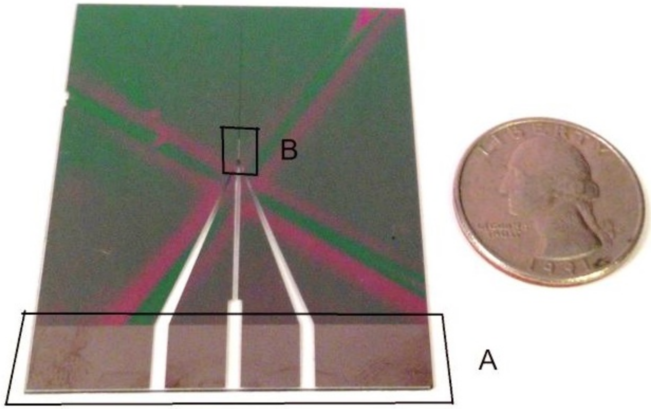
- **June 2015**: Develop fabrication process of micro-N-line probe and demonstrate method by testing two candidate electrode materials. *Complete*
- **Sept 2015**: (Go/No-Go) Discontinue dynamic particle-packing (DPP) model if predictions are not suitable match to real electrode materials. *Decision: Go*
- **Dec 2015**: Demonstrate that the DPP model can accurately imitate the mechanical calendering process for a representative electrode film. *Complete*
- **Mar 2016**: Develop a robust numerical routine for interpreting N-line conductivity measurements. *Complete*
- **June 2016**: (Go/No-Go) Continue work on N-line probe and inversion routine if method can accurately determine anisotropic conductivity. *On track*
- **Sept 2016**: Demonstrate correlations between DPP modeled conductivities and those determined by FIB/SEM and N-line probe. *On track*

# APPROACH

- Construct novel micro-N-line surface probes that can sample local conductivity of intact battery electrodes. The method overcomes multiple problems with previous methods, allowing reliable measurements of:
  - Bulk film conductivity while electrode still attached to metallic current collector
  - Contact resistance to current collector
  - Effects of pressure and presence of electrolyte
  - Spatial variations and anisotropy
- Construct a particle-dynamics model that can predict electrode microstructure and conductive pathways. The model will uniquely:
  - Predict effects of fabrication variables (slurry composition, drying, calendering, etc.)
  - Be validated with extensive experiments

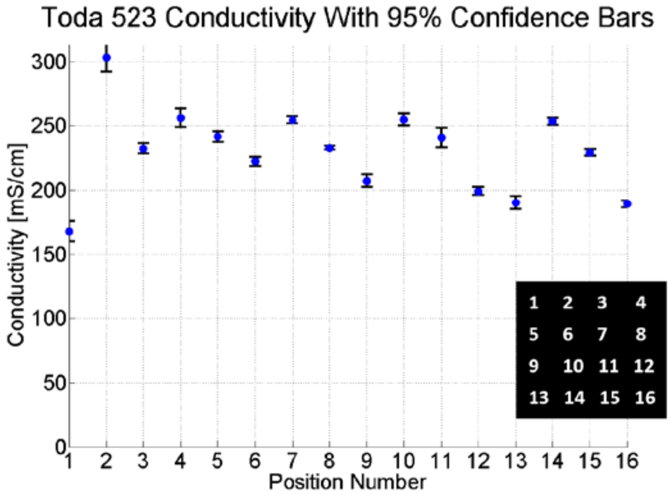
# Previous Technical Accomplishment (FY 2013): Four-Line-Probe Fabrication and Measurement

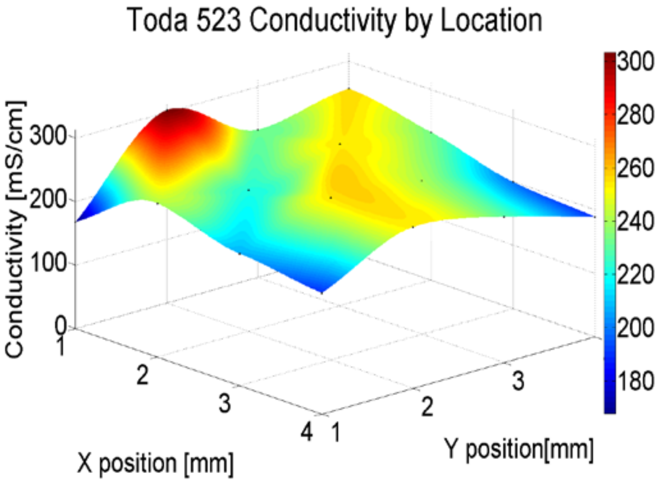




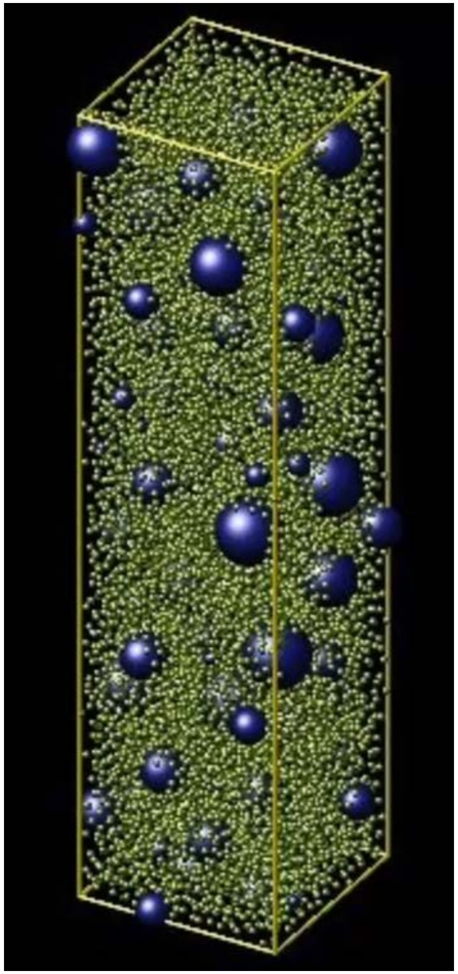

Completed micro-four-line-probe showing: (A) exposed connection pads, and (B) window for exposing the four contact lines.

- Micro-four-line-probe was fabricated in the BYU Cleanroom with conducting lines 10 microns apart.
- Because the spacing of the contacts is on the order of the cathode material thickness, the probe current probes the cathode material conductivity properties *without* large amounts of shunt current passing through the current collector metal film.



# Previous Technical Accomplishment (FY 2015): Particle Model to Simulate Electrode Drying

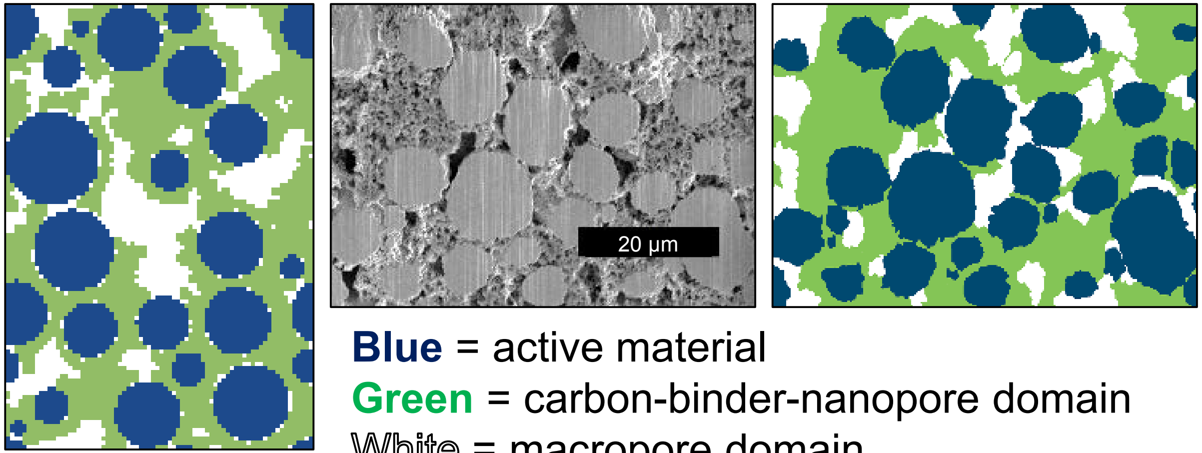


During drying the carbon particles (green) become more attractive to each other and to the active material (blue)

Shrinkage Ratio

| Film | Exp | Sim |
|---|---|---|
| Carbon | 8.6 | 8.2 |
| Active+C | 3.3 | 2.6 |

Simulated cross section (left) compared to experimental results. The SEM/FIB image (center) is segmented (right) using computer tools developed at BYU.

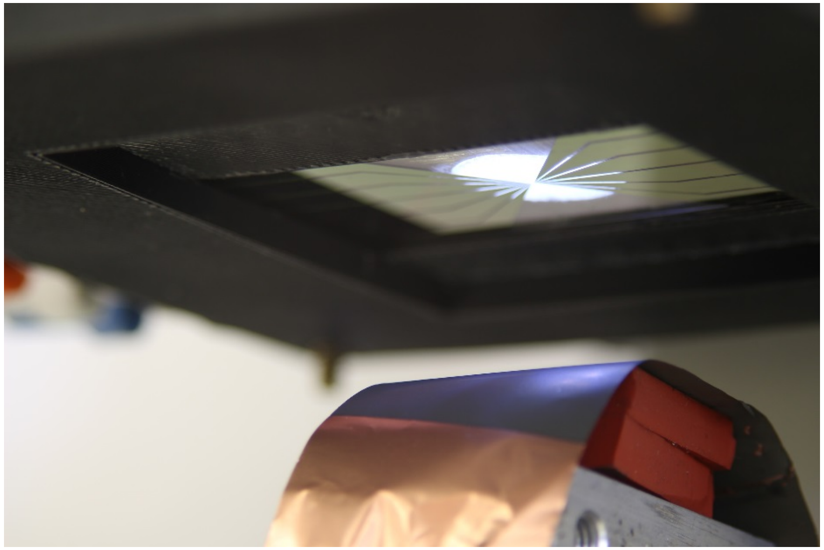



**Blue** = active material
**Green** = carbon-binder-nanopore domain
White = macropore domain

# Technical Accomplishment (FY 2016): 6-Line Probe and Improved Fixture



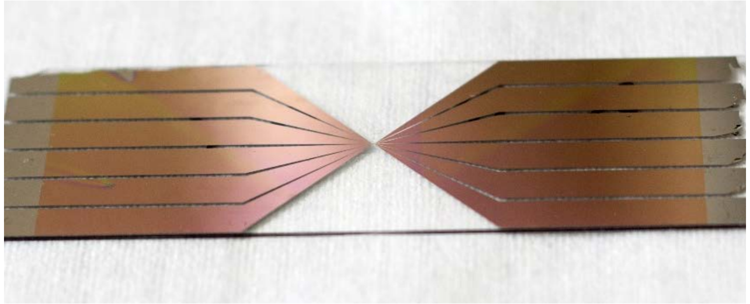
## Probe Fixture



- Using a high-precision computer-controlled stage and an integrated digital microscope we can take accurate localized measurements of battery electrode conductivity. An improved switching system increased speed of data collection.

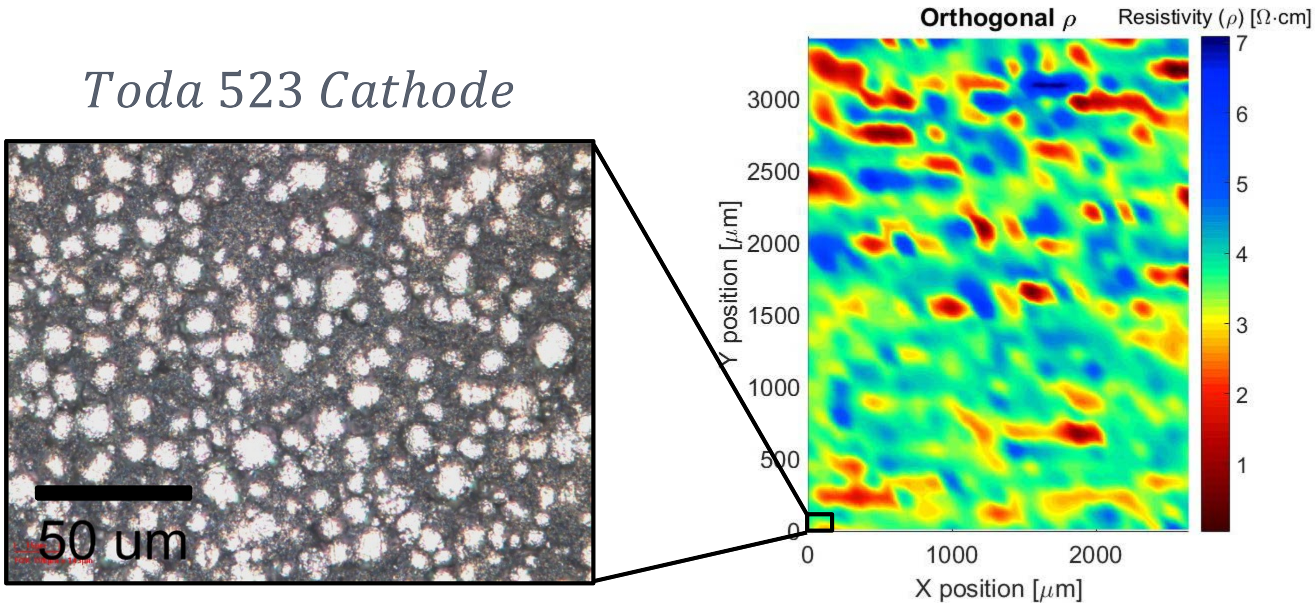
- Compared to the previous device, the new 6-line probe is more robust, allows more rapid data collection, and allows investigation of anisotropy in conductive properties. Transparency allows optical positioning of the device relative to the sample.

## 6-Line Device



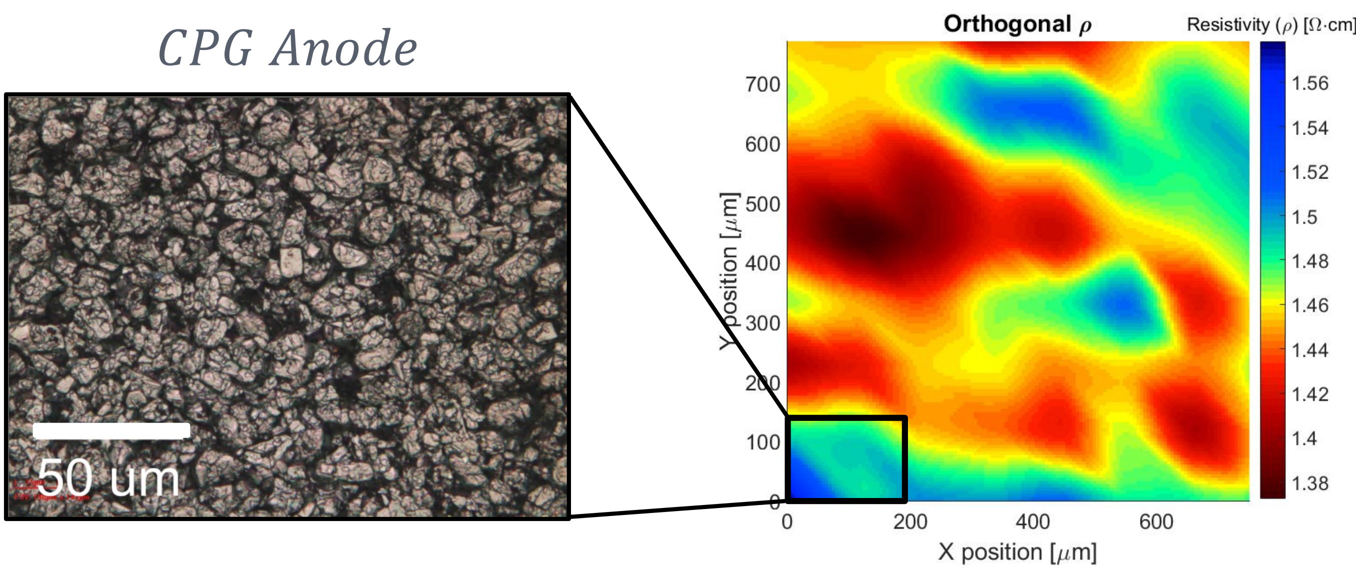
# Technical Accomplishment (FY 2015): Measurements on ANL Materials

*Toda 523 Cathode*




Electrodes from Argonne National Labs were tested. As shown, cathodes normally have a much higher conductivity deviation than anodes.

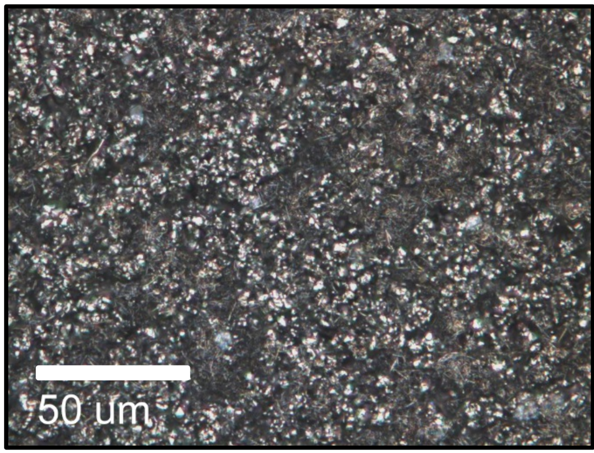
*CPG Anode*

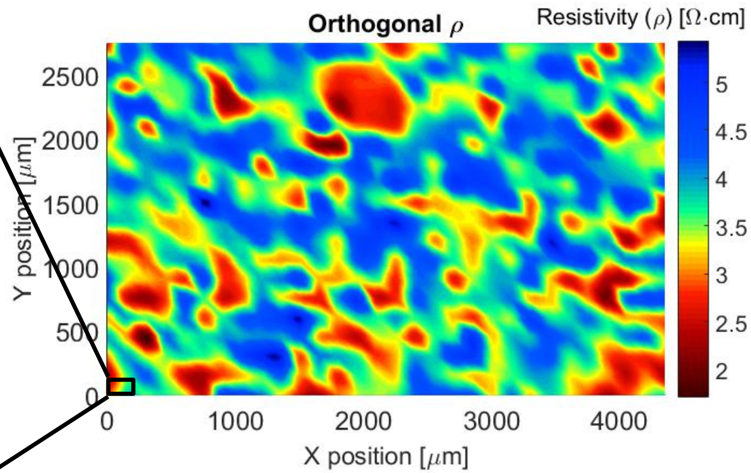


# Technical Accomplishment (FY 2015): Measurements on Hydro-Quebéc Materials



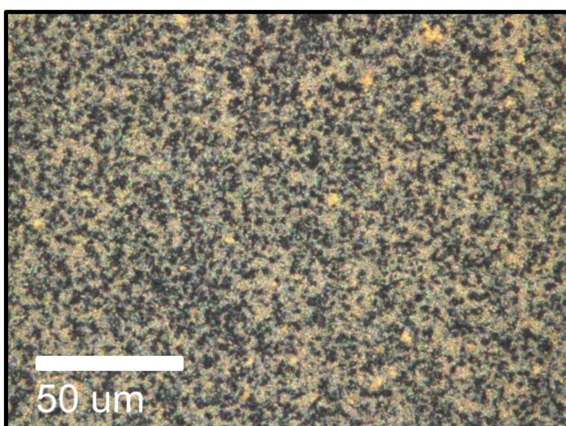
*$LiNiMnO_4$ Cathode*

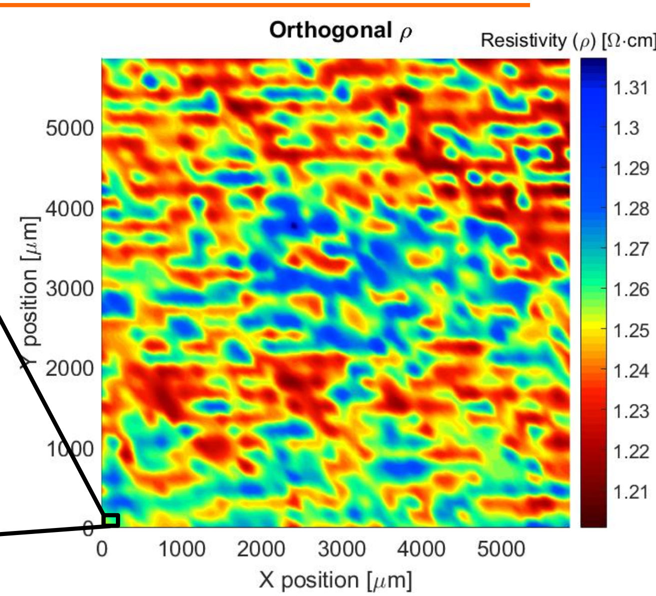



Two electrodes from Hydro-Québec were tested and showed similar results to other commercial electrodes.

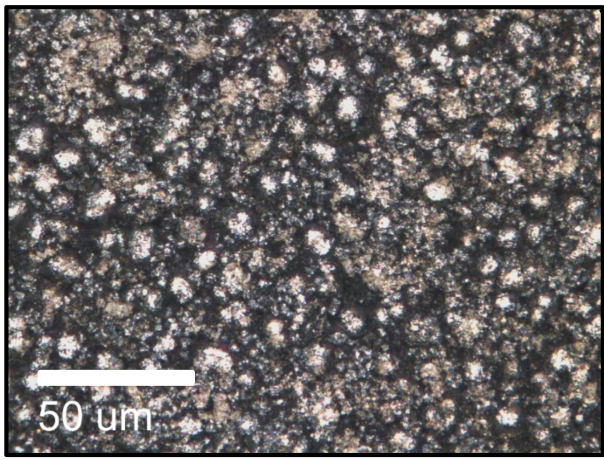
*Si Anode*

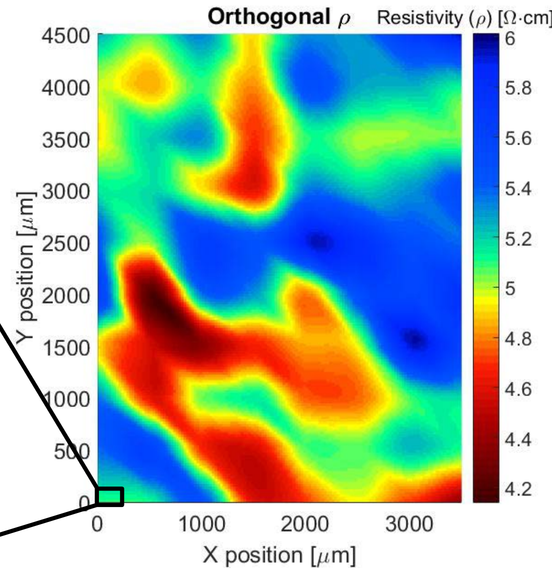


# Technical Accomplishment (FY 2016): Additional Measurements

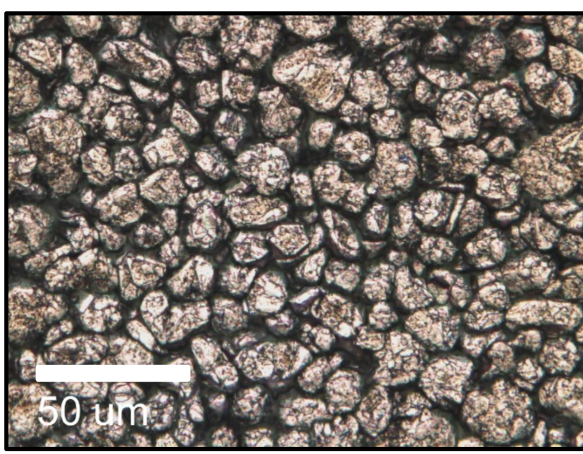
*Cathode*

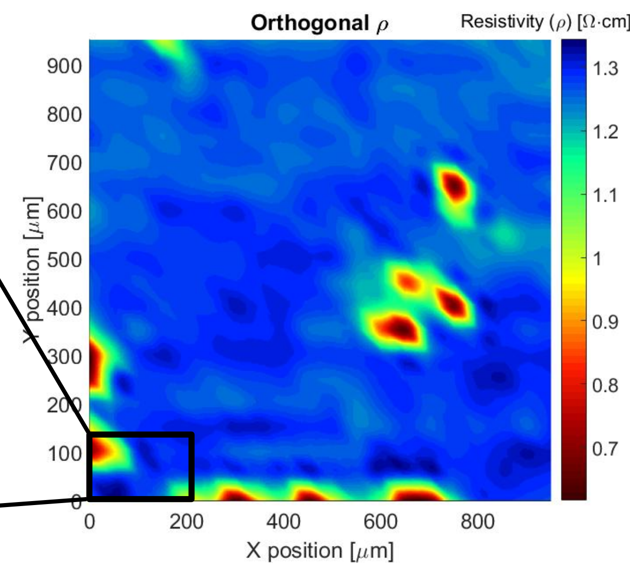



Other commercially available electrodes were tested. The anode shows some conductivity "Hot" spots.

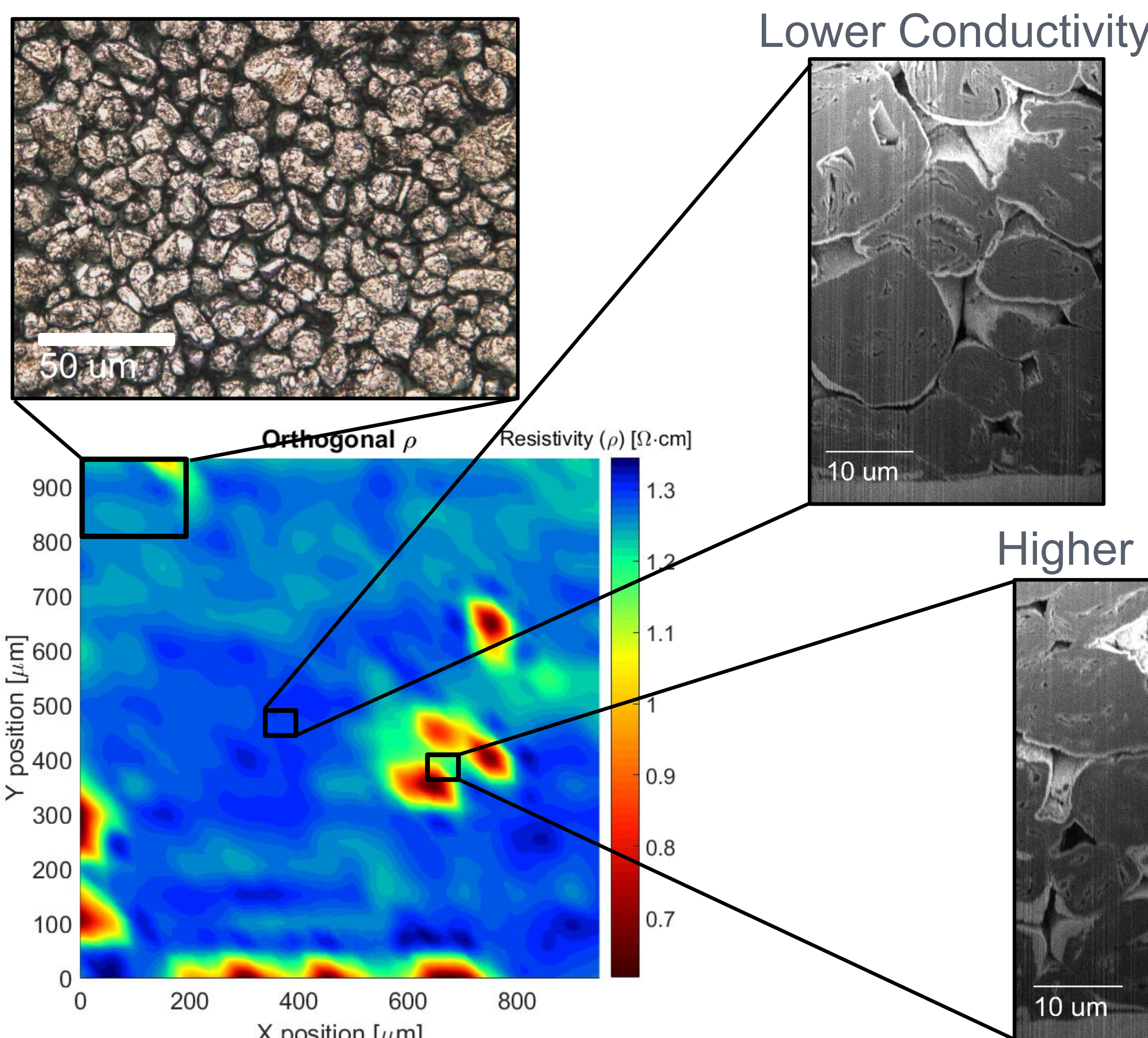
*Anode*



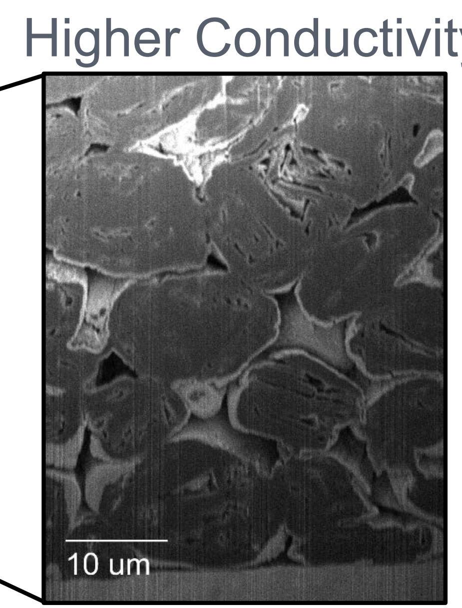



# TECHNICAL ACCOMPLISHMENT (FY 2016): HIGH-RES ELECTRODE LOCALIZATION





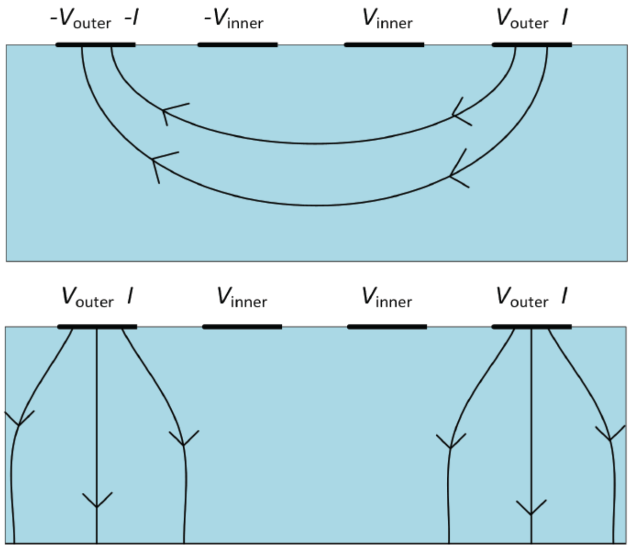

Shown here are preliminary results from a new effort to correlate local microstructure with locally measured conductivity.



# TECHNICAL ACCOMPLISHMENT (FY 2016): ANISOTROPIC INVERSION PROCEDURE



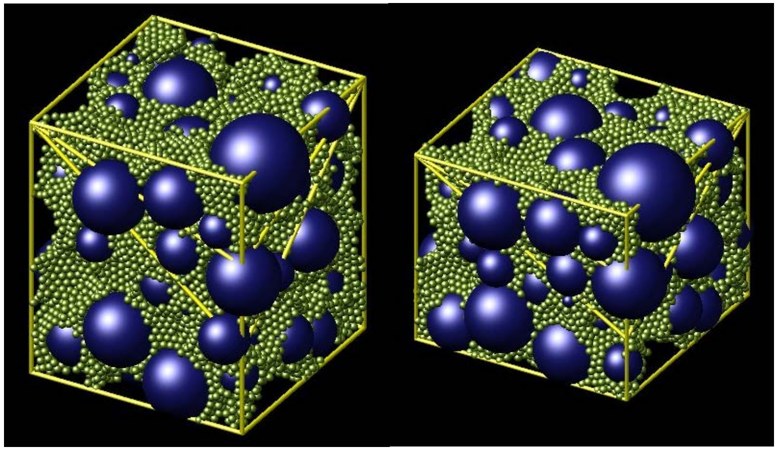
- A hybrid **analytical-numerical** inversion procedure was created and further improved to enable **accurate real-time inversion of N-line measurement data**, including anisotropy in conductive properties.
- Anisotropy of electrode materials has been detected (conductivity is higher in-plane than out-of-plane), but a satisfactorily accurate determination of the degree of anisotropy is still in progress. It was found that the anisotropic measurement is confounded by variations in contact resistance with the current collector.



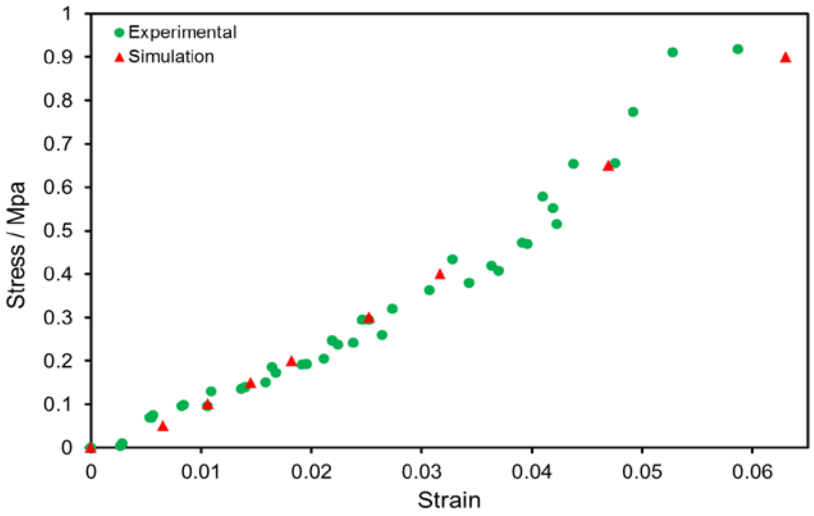

A series of tangential-type (top) and orthogonal-type (bottom) electrical measurements with realistic 3D boundary conditions is simultaneously inverted

# Technical Accomplishment (FY 2016): Particle Simulations of Electrode Calendering

The DPP model was modified to improve its ability to predict the electrode film's response to calendering, to complement previous simulations of slurry mixing and drying operations. The same model is used for all operations.



(Right) Sequential snapshots from a simulation of a Toda 523 film, showing reduction in porosity as calendering stress (vertical direction) is increased

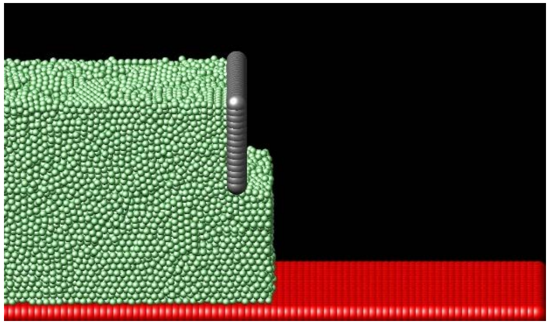



(Left) Stress-strain calendering data for Toda 523 cathode film. Both experimental and DPP model results are indicated. Experiments were performed on 4 different films by sequentially increasing the stress

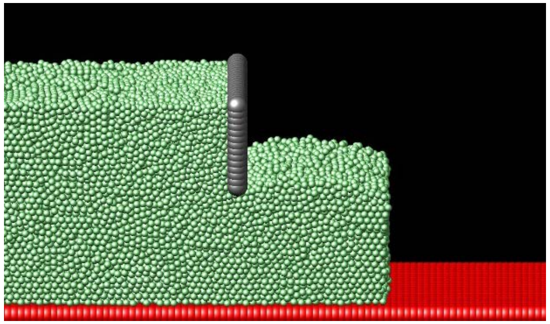
# Technical Accomplishment (FY 2016): Preliminary Simulations of Coating Process



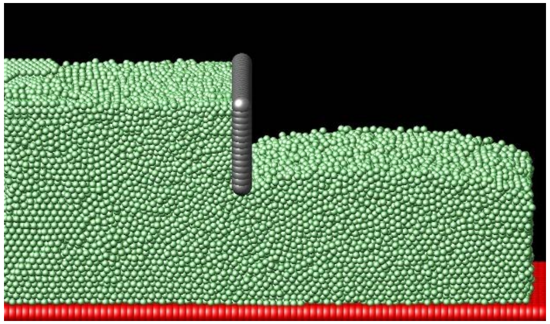
- Sequence of images (right) shows simulated electrode coating process with slurry film (green) moving relative to blade (gray)
- Slurry coating is taking place at shear rate 250 $s^{-1}$, similar to commercial operations
- To enable this, the DPP model was modified to enable liquid/gas and liquid/solid interfaces



$\Delta t$ = 0 ms



$\Delta t$ = 3.5 ms



$\Delta t$ = 7.6 ms

# Responses to Previous Year Reviewers' Comments



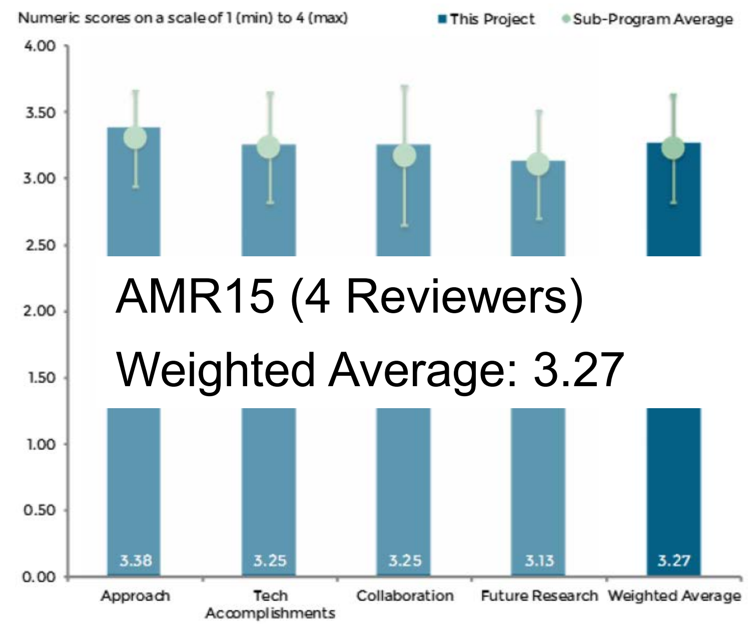
This project was favorably reviewed during AMR15 with generally positive comments. Three main concerns:

1. Modeling limitations:

   The modeling components of this project are indeed very ambitious and therefore challenging. Model variants that rely less on the specific conditions of the baseline materials are being developed for more general use.

2. Implementation in on-line operations and collaboration in commercial settings:

   While the probe is not yet able to perform commercial on-line inspection, the technology has been continuously improved to improve speed and reliability. As noted in comments last year, the project has produced interest from industrial partners – Bosch and LG Chem are new partners this year.




3. Links to real-world performance:

   Indeed the goal of this project is to link the model-predicted morphology and the conductivity measurements to real-world performance. As noted by one reviewer, there is growing realization that heterogeneity in battery structures is a problem. Our newly developed tools can quantify this and assist in quality-control efforts

# COLLABORATIONS AND COORDINATION

- Non-contract **commercial partnerships**, in which our probe technology has been used to investigate manufactured battery materials:
  - **A123**
  - **LG Chem**
  - **Bosch**
- Non-contract **research collaborations** within the battery research community, involving exchange of materials and expertise:
  - James Claypool, Missouri S&T
  - Bryant Polzin and Daniel Abraham, ANL
  - Vince Battaglia, Venkat Srinivasan, and Gao Liu, LBNL
  - Karim Zaghib, Hydro-Québec
  - Simon Theile, Univ. of Freiburg / IMTEK

# Remaining Challenges and Barriers

- Complete the development of a predictive 3D microstructure model that is validated with
  - Experimental conductivity data
  - Experimental microstructure data
- Complete measurements on additional laboratory and commercial electrodes to quantify
  - Natural spatial variations in conductivity in various material systems
  - Processing conditions and material systems that result in better uniformity of electrode films
- Success in the above two areas will provide a suite of tools for optimizing fabrication processes of particle-based electrodes.

# PROPOSED FUTURE WORK (MILESTONES)

- **June 2016:** (**Go/No-Go**) Continue work on N-line probe and inversion routine. *Justification:* While the initial four-line probe has been successful, whether or not the additional lines and inversion algorithms are satisfactory will be verified.
- **Sept 2016:** Demonstrate correlations between DPP modeled conductivities and those determined by FIB/SEM and N-line probe. *Justification:* This step begins to link the microstructural modeling and measurements to provide a more complete picture of the battery electrode manufacturing process.
- **Dec 2016:** Demonstrate the use of the DPP model to better understand microstructural changes during the coating process. *Justification:* This will be an additional predictive capability introduced in the model that enhances fundamental understanding of the coating process and the resulting microstructure that results from the high-shear-rate flow characteristic of industrial processes.
- **Mar 2017:** Provide industrial collaborators with conductivity maps based on N-line probe to assist them in improving their manufacturing processes. *Justification:* This final milestone will demonstrate to the advanced battery community the utility of the methods supported by this work and their direct applicability to improving manufacturing processes.
- This project ends April 1, 2017.

# SUMMARY

- Deliverables after third year of project
  - A single particle-based model (DPP) that can simulate a range of critical fabrication processes including mixing, coating, drying, and calendering in order to predict microstructure.
  - N-line conductivity probe that allows improved measurements, durability, and localization of conductivity "hot spots", which has begun to allow correlation of local morphological differences with conductivity differences.

- How this will improve battery manufacturing
  - Commercial-grade electrodes have significant spatial differences in conductivity due to variability on the mm and smaller length scales.
  - Our suite of tools can quantify these differences and relate them to fabrication parameters. With improved understanding, manufacturers will be able to improve electrode utilization and cycle life.